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## **Controlling Atomic Layer Deposition of TiO<sub>2</sub> in Aerogels through Surface Functionalization**

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This report demonstrates a chemical functionalization method for controlling atomic layer deposition (ALD) of  $\text{TiO}_2$  in low-density nanoporous materials. Functionalization of silica aerogel with trimethylsilane is shown to strongly suppress  $\text{TiO}_2$  growth via ALD. Subsequent modification of the functionalization through selective removal of the hydrocarbon groups reactivates the aerogel towards  $\text{TiO}_2$  deposition. These results demonstrate the potential use of ALD as a selective tool for creating novel nanoporous materials.

Nanoporous materials present significant technological advantage for a wide range of applications, including catalysis, energy storage and conversion, nanoelectronics to name just a few (1-4). Hence, there is considerable interest in developing synthetic pathways for the fabrication of nanoporous materials with tailored properties. Aerogels (AGs) are unique low-density, open-cell porous materials consisting of submicrometer pores and ligaments that can be used as a robust material platform for designing novel nanoporous materials. In recent years, a synthetic approach based on ALD on AG templates has emerged as a promising method for the directed growth of nanoporous materials (5-11, 18). This approach has been used successfully to prepare millimeter-sized high aspect ratio aerogels coated uniformly with zinc oxide ( $\text{ZnO}$ ), tungsten (W) and alumina ( $\text{Al}_2\text{O}_3$ ) (10, 11).

The ALD process utilizes two sequential, self-limiting surface reactions resulting in a layer-by-layer growth mode. The self limiting nature of the surface reactions makes ALD a particularly suitable technique for uniform deposition onto high aspect ratio porous substrates. Additionally, chemical specificity of the surface reactions in ALD enables one to control the deposition process through selective functionalization of the substrate

surface. In fact the functionalization of planar substrates such as silicon wafers with organosilane groups ( $R_nSiX_{4-n}$  ( $n = 1-3$ )) has been shown to deactivate the substrate towards  $ZrO_2$ ,  $HfO_2$ ,  $ZnO$ , and  $TiO_2$  ALD processes (12-16). A possible mechanism for the deactivation effect is the blocking of surface functional groups, such as hydroxyl (OH) moieties, which serve as chemisorption sites for the ALD precursors and hence are essential for nucleating the deposition process. Henceforth, we shall refer to these surface functional groups as nucleation sites for the ALD process.

All previous reports on the use of organosilane functionalization of surfaces to control ALD have focused exclusively on two dimensional planar substrates such as silicon wafers (12-16). However, the use of organosilane functionalization presents an attractive approach for controlling ALD in three dimensional (3D) high aspect ratio nanoporous substrates such as AGs. Selective deposition onto a substrate can be achieved by controlling the deactivation and subsequent reactivation of the substrate towards deposition in a systematic manner. In this communication, we demonstrate that the reactivity of  $SiO_2$  AGs toward  $TiO_2$  ALD (17, 18) can be switched off and on by controlling the functionalization of the AG ligament network. Specifically, we demonstrate (i) the passivation of  $SiO_2$  AGs by the capping of nucleation sites with trimethylsilyl (TMS) groups and (ii) subsequent reactivation of the AG through selective removal of the methyl capping groups by heat or oxygen plasma treatment.  $TiO_2$  was chosen as the growth material in our study because of its significance as a photocatalyst with promising energy and environmental applications (18-21). The synthetic approach presented here can potentially be extended in future to create 3D patterned nanoporous solids, for instance through spatial localization of the reactivation process.

Amorphous SiO<sub>2</sub> AGs with monolith densities of ~120 mg/cm<sup>3</sup> were used in this study. The aerogel templates, with pores and ligaments on tens of nanometers length scale, were synthesized as described in detail elsewhere (22). TMS functionalization of SiO<sub>2</sub> AG was achieved by exposure of the wet SiO<sub>2</sub> gels to chlorotrimethylsilane (CTMS) prior to supercritical extraction. Specifically, the wet SiO<sub>2</sub> gels were subjected to consecutive solvent exchanges in ethanol (48 hrs) and hexane (24 hrs), followed by exposure to CTMS solution (50 wt% in hexane) for 72 hours to promote functionalization. The functionalized wet gels were then subjected to further solvent exchanges in hexane (24 hrs) and ethanol (24 hrs) before being dried by supercritical carbon dioxide to form the aerogel.

TiO<sub>2</sub> ALD on centimeter-sized AG monoliths was performed through alternating exposures to titanium tetrachloride (TiCl<sub>4</sub>) and water (H<sub>2</sub>O) in an ALD reactor at a sample stage temperature of 100 °C and a reactor wall temperature of 125 °C. Note that TiCl<sub>4</sub> is a very reactive precursor, and thus well suited to test the degree of surface passivation. Growth of TiO<sub>2</sub> on planar SiO<sub>2</sub> substrate via ALD under similar conditions has been demonstrated previously (23). To increase heat transfer from the sample stage to the AG monoliths, hot wall conditions were replicated by placing the monoliths inside a machined aluminum container with a perforated lid. The container was then placed inside the reactor directly on the heated stage. The SiO<sub>2</sub> AG templates with and without CTMS functionalization were exposed to 5 ALD cycles simultaneously. Each cycle consisted of a 30 s TiCl<sub>4</sub> pulse followed by a 120 s dry nitrogen (N<sub>2</sub>) purge, and a 30 s H<sub>2</sub>O vapor pulse followed again by a 120 s N<sub>2</sub> purge. For planar SiO<sub>2</sub> substrates, similar deposition conditions resulted in TiO<sub>2</sub> growth rate of ~ 0.5 Å/cycle. Deposition of TiO<sub>2</sub> onto the

AGs was examined by Rutherford backscattering spectrometry (RBS) with 2 MeV  $^4\text{He}^+$  ions backscattered to  $164^\circ$  and by synchrotron based X-ray fluorescence (XRF) measurements at the Advanced Photon Source. In RBS measurements depth uniformity of the deposited Ti concentration was determined based on RUMP code (24) simulations, as described in detail elsewhere (25). In RUMP simulations, the composition of the AG ligaments following  $\text{TiO}_2$  deposition was defined as  $\text{SiO}_{2(1+x)}\text{Ti}_x$ . Surface area of the AGs prior to deposition was measured using the Brunauer-Emmett-Teller (BET) method. Morphology of the resulting  $\text{TiO}_2/\text{SiO}_2$  nanocomposites was characterized in a Philips FEG-300 transmission electron microscope (TEM).

A schematic outline of our approach to deactivation and subsequent reactivation of the  $\text{SiO}_2$  AG template towards  $\text{TiO}_2$  ALD is shown in Fig. 1. Chloro-organosilane deactivating agents are known to react with surface OH groups, leaving alkylsilyl groups bonded to the surface through covalent Si-O bonds (16). Therefore, deactivation of the  $\text{SiO}_2$  AG template by TMS is expected to occur by the following two mechanisms: 1) silylation of the reactive surface OH groups and 2) steric blocking of the  $\text{SiO}_2$  surface by TMS groups since  $\text{TiO}_2$  nucleation is believed to be possible at the Si-O-Si sites as well as the surface hydroxyl groups (15, 17).

Functionalization of the AG network with TMS drastically reduces  $\text{TiO}_2$  deposition on the AG, as evident from the RBS results shown in Fig. 2. The RBS measurements give Ti atomic concentrations of 1.9 % and 9.5% for TMS functionalized and non-functionalized AGs, respectively. This corresponds to a 5 times lower  $\text{TiO}_2$  deposition on the TMS functionalized AG. In both cases,  $\text{TiO}_2$  deposition is uniform upto a depth of  $\sim 20$  microns (the maximum depth probed in our RBS analysis for the 120

mg/cm<sup>3</sup> AG). Deactivation of the AG by TMS functionalization has also been confirmed by our XRF measurements wherein the Ti fluorescence signal, following TiO<sub>2</sub> ALD, from the functionalized AG is minimal compared to the non-functionalized AG. Similar TiO<sub>2</sub> deposition behavior was also observed in the case of lower density, 20 mg/cm<sup>3</sup>, AG templates under identical deposition conditions. We expect that our surface passivation would be even more effective for less reactive ALD precursors such as the [Ti(OPr<sup>i</sup>)<sub>4</sub>] precursor used by Park *et al* in their work involving planar silica substrate (14). Further optimization of the deactivation effect may also be possible through experimentation with different functional groups as the deactivating agent.

Specific surface areas of the SiO<sub>2</sub> AG monoliths used in our study are given in Table 1. Interestingly, the TMS functionalized SiO<sub>2</sub> AG has a larger surface area relative to the non-functionalized AG. Functionalization of the SiO<sub>2</sub> AG with hydrophobic TMS groups is known to inhibit unwanted condensation reactions within the wet gel (26). This in turn may help to minimize any associated loss in AG surface area due to cross-linking of the AG ligaments during the wet gel stage. In our experiments there was a lag period between the synthesis of the wet gel and the subsequent supercritical extraction of the AG. In case of the non-functionalized wet gel, additional condensation reactions during the lag period most likely accounts for its lower surface area compared to the functionalized AG. Measured surface area of the functionalized AG in our experiments is in good agreement with the surface area reported by Schwertfeger *et al* for 160 mg/cm<sup>3</sup> TMS functionalized SiO<sub>2</sub> AG (27). Alternatively, it is possible that TMS functionalization leads to roughening of the AG ligament surface with a resultant increase in the overall AG surface area. It is important to note that, independent of the origin, the increased



surface area of the functionalized aerogels results in an underestimation of the effectiveness of the TMS passivation. Accounting for the roughly three times higher surface area of the functionalized aerogels, the presence of trimethylsilyl capping groups suppresses the deposition of  $\text{TiO}_2$  by a factor of 15 rather than 5. This highlights the significance of surface nucleation sites in the ALD growth process and the role played by TMS in the deactivation of these nucleation sites.

Fig. 3 shows bright-field TEM images of the  $\text{SiO}_2$  AGs before and after  $\text{TiO}_2$  ALD and of the TMS functionalized AG after ALD. The ligament width for both the functionalized and non-functionalized AGs before ALD is  $\sim 8\text{-}10$  nm (Fig. 3A). The deposited  $\text{TiO}_2$  is not readily distinguishable from the underlying  $\text{SiO}_2$  substrate since the TEM images of the untreated and  $\text{TiO}_2$ -coated AGs do not show any detectable differences in their ligament size. Therefore, based on the observation that  $\text{TiO}_2$  deposition does not lead to any obvious change in the AG ligament morphology, the overall AG surface area following deposition is not expected to change under these conditions. Area-selective TEM-EDX analysis of the AGs following deposition further confirms the significant difference in  $\text{TiO}_2$  content between the functionalized and the non-functionalized AGs (Fig. 3D, E). For the non-functionalized AG the Ti/Si ratio was found to be nearly independent of the size of the analyzed area ranging from larger sample fragments down to the single ligament level. In comparison, hardly any Ti signal was detected from the ligaments of the functionalized AG. These results are consistent with our RBS and XRF data, suggesting that  $\text{TiO}_2$  growth requires the presence of chemisorption sites for the ALD precursors.

Next, we evaluated different sample treatments in terms of their effectiveness in reactivating the TMS functionalized SiO<sub>2</sub> AGs towards TiO<sub>2</sub> ALD. The objective was to selectively remove methyl (CH<sub>3</sub>) capping groups with minimal perturbation of the AG architecture. We exposed the TMS-capped AG to one of the following two reactivation treatments: 1) heating in a tube furnace at 325° C in air for 8 hours, or 2) oxygen plasma exposure in a Branson /IPC Asher (300 watts, 80 sccm, 44 mTorr) for 3 minutes. Following the reactivation treatment AG samples were exposed to 5 cycles of TiO<sub>2</sub> ALD. RBS measurements gave Ti atomic concentrations of 6.0 % and 10.7% for heat and plasma treated AGs, respectively (Fig. 2). By comparison Ti atomic concentrations for the non-functionalized and functionalized AGs without the reactivation treatment were 9.5 % and 1.9 %, respectively (Fig. 2). The Ti atomic concentration for the plasma treated AG is ~2 times greater than the heat treated sample. Therefore, oxygen plasma exposure is the more effective of the two treatments in restoring reactivity of the TMS functionalized AG towards TiO<sub>2</sub> ALD. Neither plasma nor heat treatment resulted in the loss of AG surface area. Hence the reactivation treatments appear to have minimal impact on the overall AG architecture.

Both reactivation approaches described above rely on the oxidative degradation of the organic capping groups (28). For example, the use of oxygen plasma to remove hydrocarbon resists is a well established technique in microelectronic device fabrication (29). The reactivation process restores the original surface chemistry as it leaves the substrate functionalized with OH groups. However, the authors want to point out that the reactivation treatment does not remove the intact trimethylsilyl capping group, but leaves an additional Si atom per capping group behind. Compared to thermal oxidation, the

availability of reactive species (i.e. atomic oxygen) in the plasma seems to enhance the degradation process (28). Surprisingly, plasma treatment is successful in reactivating the AG up to a depth of  $\sim 20$  microns, the maximum depth probed in our RBS analysis for the  $120 \text{ mg/cm}^3$  AG. This observation suggests that the plasma induced reactivation mechanism is not limited to line of sight etching by plasma generated reactive species. It is possible that atomic oxygen has a low sticking and recombination probability in  $\text{SiO}_2$  AG, thus allowing for its penetration into the pores of the AG and the resultant re-activation of sub-surface active sites. It is also plausible that these reactive species are generated in situ *within* the pores of the AG by penetration of the plasma inside the non-conductive and nanoporous network and thereby promoting bulk reactivation. However, further studies need to be done in order to verify this hypothesis.

In summary, we have shown that functionalization of a  $\text{SiO}_2$  AG template with organosilane groups inhibits  $\text{TiO}_2$  ALD on the high aspect ratio nanoporous structure. This approach can possibly be applied to other ALD processes as well which require the presence of surface OH as nucleation sites. Additionally, we have demonstrated re-activation of the functionalized AG template for  $\text{TiO}_2$  deposition through direct removal of the hydrocarbon capping groups. The synthetic approach presented here can potentially be extended to fabricate 3D structured nanoporous materials by using direct laser writing methods to locally reactivate a passivated AG template (30, 31). For instance, photosensitive capping groups can be used to facilitate localized photoinduced reactivation of the AG. It may also be possible to take advantage of the low thermal conductivity of AGs to promote localized thermally induced reactivation by using laser light to locally heat the AG template. Dulcey *et al* have already demonstrated the

feasibility of the first approach in the case of a functionalized planar silica substrate (32). The ability to control the ALD nucleation process on nanoporous templates through selective surface functionalization constitutes an important step towards the ultimate goal of precisely engineered nanomaterials.

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